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Research Paper

Investigation of the Factors Affecting on the Granulation of ZrB_2 Nano-Particles Synthesized by Using Na Metal as Reductant

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ABSTRACT

In the present research, as the initial phase, the ZrB_2 nano-powders are synthesized at low-temperature through heating a mixture of $ZrCl_4$, B_2O_3, and Na metal in a molar ratio of 1:2:4 at 650 to 950 °C under pure argon atmosphere. The effect of various parameters involved in the phase transformation and morphology of the ZrB_2 nano-powders are investigated. Also examined systematically are the influence of the stoichiometry of the reactants and different factors bearing upon the granulation of ZrB_2 particles. In particular, we have studied the effects of adding NaCl salt as well as thermodynamic parameters playing roles in the above synthesis process. The morphology of samples is characterized with the help of scanning and transmission electron microscopy. The XRD results shows the presence of ZrB_2 single phase in the product. The obtained images indicate that the synthesized powders have a crystallite nano metric size ranging from 11 to 26 nm. The TEM images and statistical size distribution also reveal the presence of a narrow size distribution of ZrB_2 nano-particles. Also explored and reported are various enhancement parameters like temperature, reaction time, and diluent component on the quality of the synthesized ZrB_2 nano-powders.

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1. Introduction

Zirconium diboride (ZrB_2) belongs to a hexagonal system displaying a combination of Zr–Zr metallic bonds, B–B covalent bonds, and Zr–B covalent/ionic bonds [1]. Because of its specific atomic structure and chemical bonding, ZrB_2 exhibits several remarkable properties including a high melting point (3246°C), moderate thermal conductivity (60 $W \cdot m^{-1} \cdot K^{-1}$), electrical conductivity (1.0×10^7 $S \cdot m^{-1}$), high hardness (23 Gpa), good wear and corrosion resistance [2]. Given these unique properties, ZrB_2 has wide applications in refractory materials, cutting tools, crucibles, high-temperature heating elements, and coating materials for rockets and supersonic aircraft [3]. Various ZrB_2 composite materials exhibiting excellent properties have been developed enriching the application range of the substance [4–6]. Numerous synthetic procedures have been proposed to prepare ZrB_2 powders including:

(i) Solid-state reaction syntheses,
(ii) Electrochemical syntheses,
(iii) Mechanochemical syntheses,
(iv) Self-propagating high-temperature syntheses [7].

Reviewing the literature shows an urgent need for finding a more facile and cost-effective way for synthesizing fine ZrB_2 powder. There are typically several reduction methods for synthesizing these powders, including borothermal reduction [8], carbothermal reduction [9] and boron / carbothermal reduction [10]. Compared with other methods, reduction reactions are more controllable and less expensive. For this reason, during the past few years, researchers have shown great interest in borothermal reduction as there is no carbon or metal impurities in the final product. The refractory property and high stability of transition metal diborides are due to the high negative Gibbs free energy of formation, which characteristic is strongly correlated with the formation enthalpy. The changes in the standard Gibbs free energy in the reduction methods are calculated using the Fact-Sage 7.0 software [11] and is shown in Fig. 1. The results given in Fig. 1 show that reaction (2) can occur at a higher temperature than other reactions, which feature may lead to larger particle sizes of the resultant ZrB_2. By contrast, the reaction using Mg as the reducing agent occurs at a low temperature compared to other reactions. Besides, reaction (4) is always thermodynamically more desirable even at low temperatures. It is a well-known fact that low temperatures are conducive toward preparing fine-sized particles. Thus, reaction (4) is singled out as the most appropriate method for preparing ZrB_2 powders having small particle size.

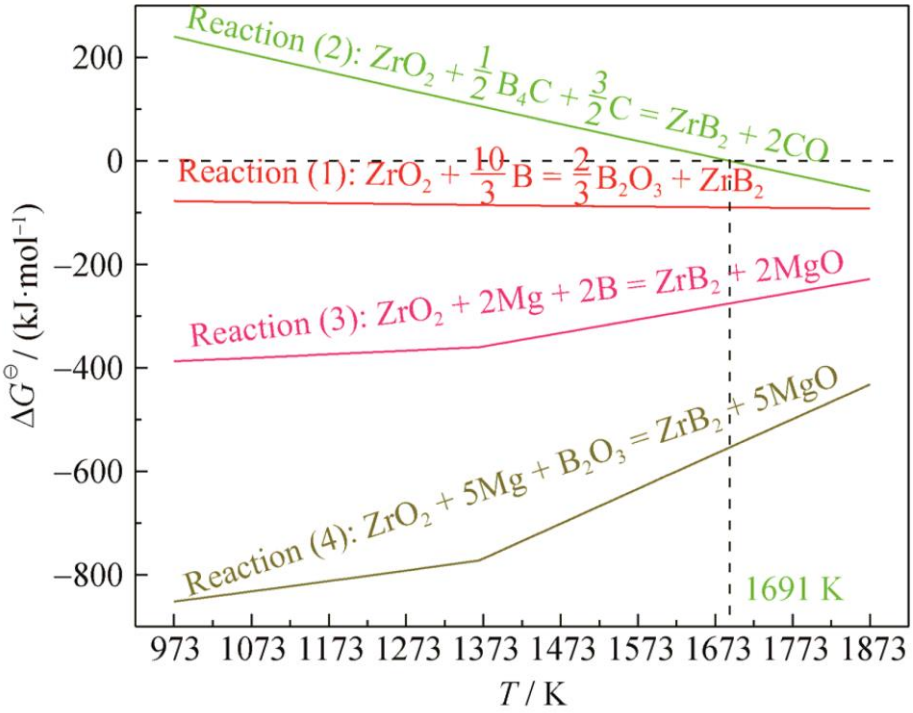


Fig. 1. Changes in standard Gibbs free energy for different reactions

Quite a number of investigations on the metal reaction method for preparing ZrB_2 powders are reported in the literature. Recently, using ZrO_2 powder with micrometer granulation as a raw material, fine ZrB2 powders with a particle size of 0.4 - 0.7 micrometers have been produced through a

new method of borothermal reduction [12]. The ZrB_2 powder is industrially produced by creating conditions for the reaction of carbon (C), zirconium oxide (ZrO_2) and boron carbide (B_4C) [13]. Andrievskii et al obtained an amorphous nano-powder of ZrB_2 with a mean particle size of 40 nm through thermal decomposition of Zr $(BH_4)_4$ at 573 - 623 ˚C. [14]. A new method consisting of a mixture of B_2O_3, ZrO_2 and Mg has been developed to prepare ZrB_2 powder at 1073 - 1373 ° C for 1 hour. In this method, despite the small amount of ZrO_2 as a minor phase in the final product, the fine powder of the single phase ZrB_2 is prepared at 1373 ˚C having been treated by a water-alcohol mixture [15]. Currently, Currently, attempts are being made to produce ZrB_2 through metallothermic reduction of ZrO_2 and B_2O_3 as main sources of Zr and B, respectively. As is noted in previous research works, ZrB_2 can be synthesized at mild temperatures by heating ZrO_2, B_2O_3 and Na metal in molar ratios of 1:5:15 at 873–1273 ˚C for 24 hours [16]. And as is indicated in the literature, Raw materials and reducing agents play an important role in ZrB_2 synthesis strategy. In most cases, by means of reagents like $LiAlH_4$ or $NaBH_4$ as reductants, some insoluble by-products such as ZrO_2, ZrH_2 and MO_X are produced as a minor phase. These products could not be eliminated through common water-alcohol purification and acid treatment procedures. So, our proposed method is designed and built upon high purity and low temperature reaction conditions. As a matter of fact, this study set it as its primary goal to explore preparation of fine ZrB_2 powders by $ZrCl_4$ and B_2O_3 as starting materials and Na metal as reducing agent at alternate temperatures of 650 to 950 ˚C based on Eq. (1) below. An additional and significant object of this study is to understand the influence of the stoichiometry of the reactants in the ZrB_2 formation process. Also investigated are as main goal of this paper, the different factors like the addition of NaCl affecting on the granulation of ZrB_2 particles as well as conducting an analysis of the effects of thermodynamic parameters on the particle size of products and the growth rate of the particles.

2. Experimental

2.1. Precursor materials

In this research, the following items are used as raw materials: Anhydrous zirconium (IV) chloride ($ZrCl_4$) (Purity: 99.8, anhydrous, Sigma-Aldrich), B_2O_3 powder (Purity: 99.5 %, Sigma-Aldrich), sodium metal (Purity: 99.0 %, pieces by Sigma-Aldrich) and**,** NaCl (Purity: 99.9 % purity, anhydrous, Sigma-Aldrich).

2.2. Syntheses of ZrB_2 nano-powders

As is expressed in Eq. (1) given below, our goal is to synthesize nanoparticles of ZrB_2 via metallothermic reduction technique at low-temperature ranges employing Na metal as a reducing agent.

$$ZrCl_4 + B_2O_3 + 10\,Na \xrightarrow{heat} ZrB_2 + 3\,Na_2O + 4NaCl \quad (1)$$

In the primary stage of research, 5 mmol $ZrCl_4$, 5 mmol B_2O_3 are mixed and placed in a BN crucible (Showa Denko, purity: 99.0 %; outer diameter: 33 mm; inner diameter: 20 mm; depth: 22 mm). Then, according to Equation (1), for the synthesis of ZrB_2 using a Na reducing agent, about 50 mmol Na metal pieces were weighed and added to the reactants and then placed in the BN plate. After preparing starting materials, they were kept in a horizontal tubular furnace (Lab Exciton Furnace, model: EX.1200.T-60) and heated for 3 hours. During the synthesis reactions, argon gas (99.999 % pure) was continuously flowing inside the furnace while the mixture was heated at several temperatures for each reaction. The heating rate was 5 ˚C/min under argon atmosphere. finally, the mixture was cooled naturally in the furnace under argon gas flow so as to obtain a black powder. The stoichiometric ratio of the raw materials in reaction (1) is $ZrCl_4$: B_2O_3 : Na = 1:2:4. In this process, the excess metal Na was removed by the reaction of 2-propanol followed by ethanol and water (alcohol–water) treatment. The powder was then leached in the hydrochloric acid (10 wt. %) at 100 ˚C for 3 hours to remove the metal oxides, by-products, and impurities (acid treatment). At last, the final product was separated with the help of a filter paper and rinsed with de-ionized water and absolute ethanol before being dried at 60 ˚C for 2 hours in an oven. The effect of adding NaCl on the synthesis of ZrB_2 powder was also investigated. The detailed experimental conditions for methallothermic reduction are displayed in Table 1.

Table 1. Experimental conditions for reduction reaction

Sample	Reagents	Molar ratio	Temperature (˚C)	Time (h)	Product
ZB-1	$ZrCl_4 : B_2O_3 : Na$ + 0 % NaCl	1 : 1 : 2	500	1	ZrB_2, ZrO_2
ZB-2	$ZrCl_4 : B_2O_3 : Na$ + 0 % NaCl	1 : 2 : 4	650	3	ZrB_2
ZB-3	$ZrCl_4 : B_2O_3 : Na$ + 20 % NaCl	1 : 2 : 4	750	3	ZrB_2
ZB-4	$ZrCl_4 : B_2O_3 : Na$ + 20 % NaCl	1 : 2 : 4	850	3	ZrB_2
ZB-5	$ZrCl_4 : B_2O_3 : Na$ + 20 % NaCl	1 : 2 : 4	950	3	ZrB_2

2.3. Characterization

The phase composition of the ZrB_2 samples were determined by X-ray diffraction analysis (XRD, Cu Kα radiation at λ = 1.54184 Å, model: Asenware AW-DX 300) in a 2θ angle ranging from 10˚ to 90˚. Microstructures and morphologies of the powders Were examined using a field-emission scanning electron microscopy (FE-SEM, FEI Quanta 200, USA, 30 KW) equipped with an energy dispersive spectroscopy (EDS) system. Transmission electron microscopy (TEM) images were obtained using a TEM (208S, Philips ,Netherlands, 100 KW) having tungsten filament as electron beam generator as well as a digital camera used for determining the phase compositions. Particle size distribution of each product was accomplished through the Image Tools software from the TEM Micrographs. The thermodynamic parameters of the mentioned reactions; namely, ΔH (change in enthalpy), ΔG (change in Gibbs free energy) were calculated using an HSC chemistry software.

3. Results and discussion

3.1. Characterization of the synthesized ZrB_2

3.1.1. XRD analysis

As mentioned above, the raw materials were mixed and heated under argon barley in the presence of sodium reducing agent at different temperatures from 500 ˚C to 950 ˚C. The process began with a synthesis of ZB-1 powder. According to the XRD pattern of the ZB-1 powder, in addition to the ZrB_2 phase, the ZrO_2 phase was detected in the ZB-1 sample; The ZrB_2 constitutes the major phase. The experimental data reveals that the heating temperature and the reaction time are not sufficient parameters (Fig. 2). Thus, the presented method was improved by changing the reaction time, furnace temperature, and molar ratios of reagents. The XRD patterns of samples of ZB-2 to ZB-5 prepared by heating the mixture of $ZrCl_4$: B_2O_3: Na with 1:2:4 mole ratios at 650, 750, 850 and 950 ˚C temperatures are shown in Fig. 2, respectively. All these patterns were recorded after being rinsed with ethanol–water and undergoing acid treatment. In the ZB-2 sample, the lowest temperature was applied for the reaction, but not withstanding the formation of pure ZrB_2, some of the final product seemed to have an amorphous structure at this temperature. As is seen in the XRD patterns of ZB-3, ZB-4 and ZB-5 at 750, 850 and 950 ˚C in Fig. 2, the ZrO_2 phase completely disappears, and some by-products are eliminated. The crystalline ZrB_2 nano-particles are obtained. Hence, as was indicated, the ZrB_2 phase is the main phase. It is interesting to note that in this research, B_2O_3 as a boron source played an important role in synthesizing ZrB_2 when it reacted with $ZrCl_4$ in the presence of Na metal as a reducing agent in a dry and inert ambient. However, in order to remove the residual ZrO_2 phase in the powders, the reaction time was increased up to 3 hours to yield a mono phase product. According to Eq. (1), as the main reaction, by increasing the ratio of B_2O_3 and Na in the starting materials, some side reactions occur. In this way, Impurities and by-products are continually removed after being rinsed and treated with acid. Thus, no sign of impurities such as ZrO_2 and MO_X is observed in the XRD patterns.

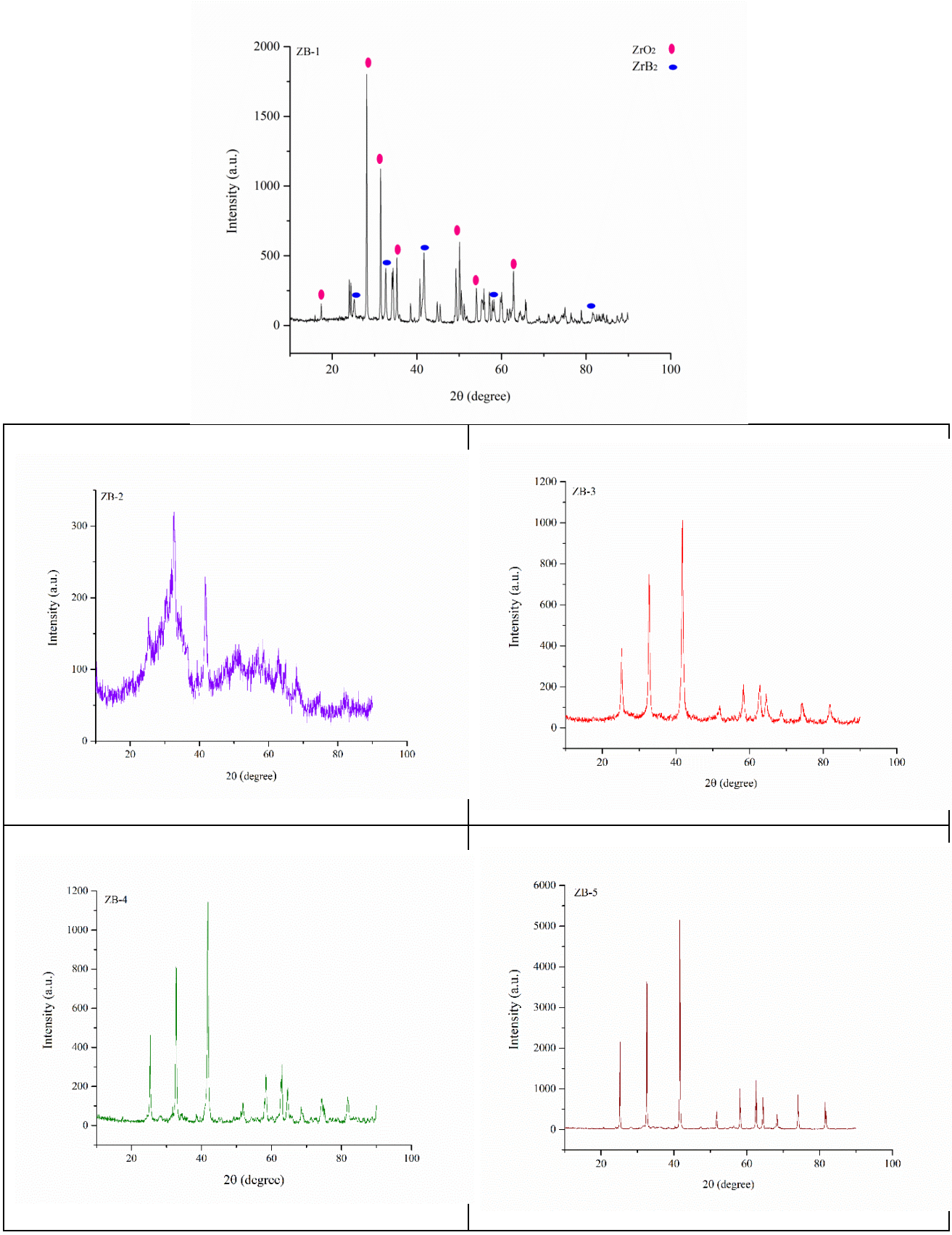
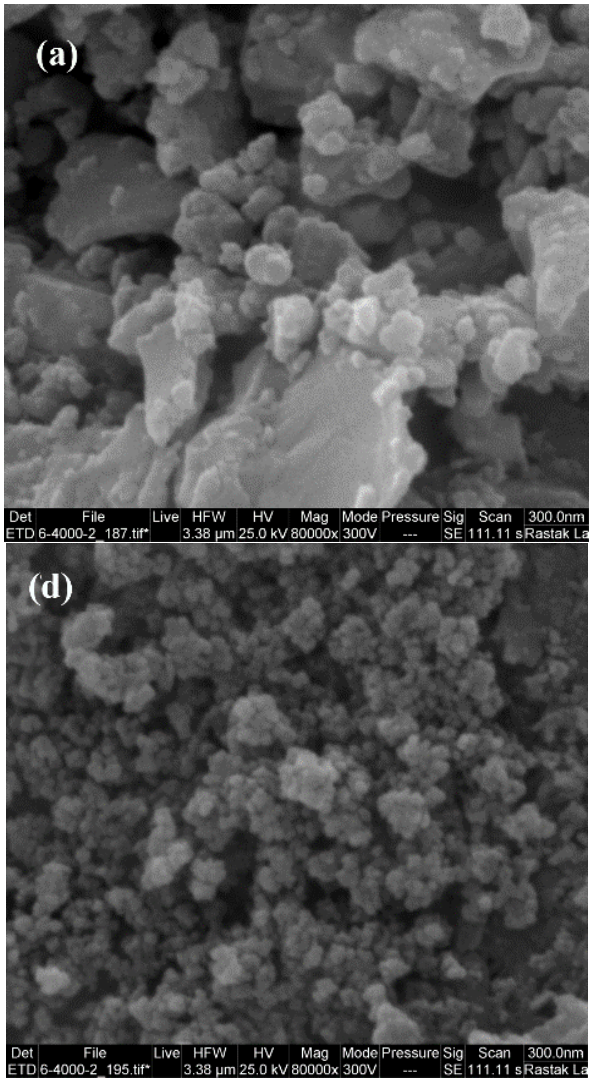
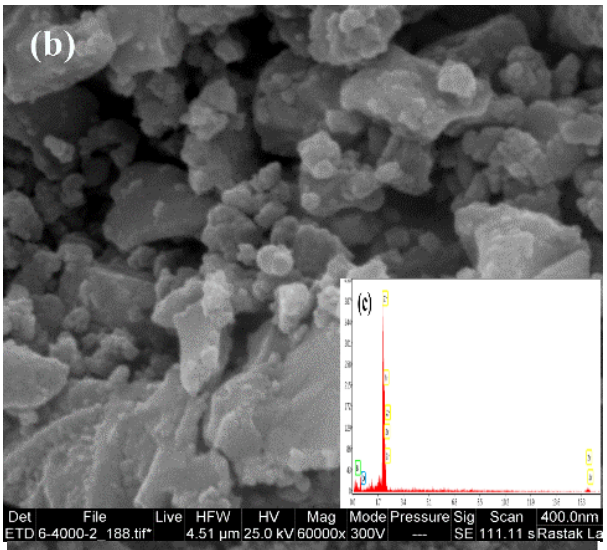


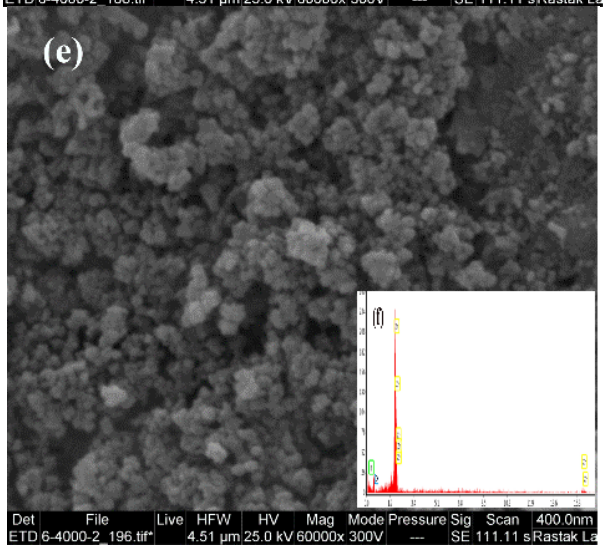
Fig. 2. XRD patterns of ZB-1 powder processed at 500 ˚C for 1 hour and prepared ZrB_2 nano powders using Na at 650-950 ˚C for 3 hours

3.1.2. The ZrB_2 nano-powders morphology

The morphological analysis of ZrB_2 nanoparticles, fabricated at different temperatures for granulation analysis is shown in Figure 3. As is seen in the SEM images, the ZB-2 sample, at 650 ˚C shows, agglomeration of quasi-spherical particles and a size distribution of nano-particles (see Fig. 3(a-b)). It can be seen that the particle sizes of the ZB-3 and ZB-4 nano-powders are much smaller than those of the ZB-2. This is indicative of the fact that the newly developed low-temperature synthesis method of ZrB_2 nano-powders could significantly reduce the particle sizes of ZrB_2 powders. The ZB-3 and ZB-4 nano-powders have narrower size distributions and more spherical morphologies than those of the ZB-2 and ZB-5 samples. As the microstructure SEM images show, fine powders are bonded together to form large aggregates. Furthermore, around these large aggregates,there are many dispersed small particles. The XRD results show that by increasing the temparature, the morphology of the obtained powders is changed.The EDS results demonstrate that the composition of the particles mainly contains the Zr and B. Combined with their corresponding XRDs, the nano-particles should produce ZrB_2.







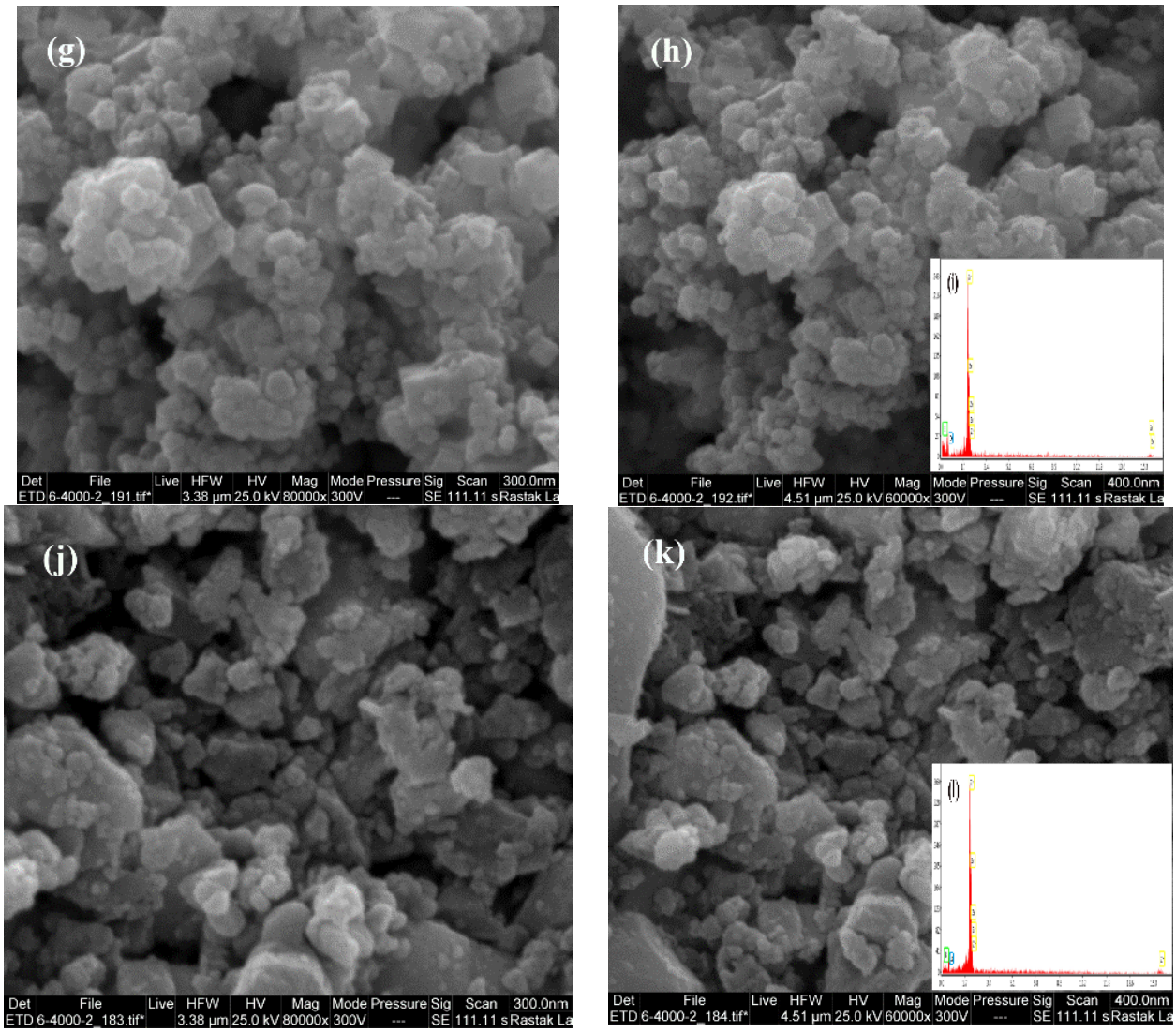


Fig. 3. Respective SEM images of ZB-2(a-b), ZB-3(d-e), ZB-4(g-h) and ZB-5(j-k) nano-powders at 300 nm and 400 magnifications; EDS micrographs ZB-2 (c), ZB-3 (f), ZB-4 (i) and ZB-5 (l).

The size distribution and microstructure of the synthesized ZrB_2 nano-particles are characterized by TEM. Fig. 4. The average diameter of the ZB-2 grains is 26 nm at 650˚C, Fig.4 (a-b). The ZB-3 powders show the agglomeration of spherical nano-particles. According to the statistical histogram data, Fig. 4 (d-e), the average diameter of the ZB-3 crystallites is 11 nm at 750 ˚C. Fig. 4(g-h), illustrates the TEM images of the ZB-4 nano-powders at 850 ˚C, revealing that at higher temperature, the crystallite size of the major phase increases with a hexagonal structure. The histogram of particle size distribution shows the average size of ZB-4 grains at about 19 nm at 850 ˚C. As is illustrated in Fig. 4(j-k), the ZB-5 sample has a spherical shape with an average crystallite size of 17 nm. The TEM images of these samples indicate the combination of individual particles as a whole, vividly defining the grain sizes. As is seen in the TEM images, the ZrB_2 samples appear to have spherical and hexagonal morphologies.

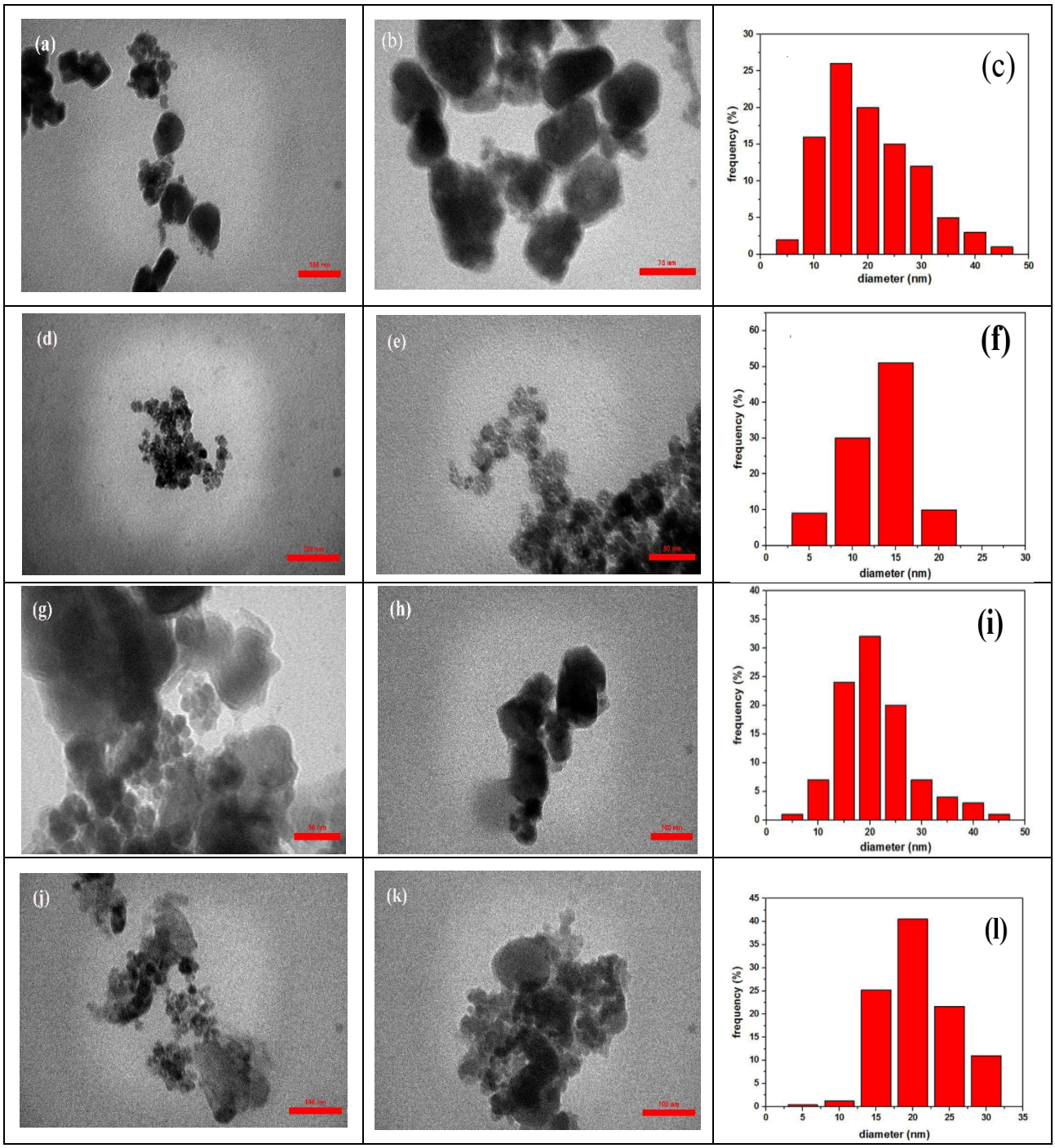


Fig. 4. TEM images of ZB-2(a, 100 nm & b, 75 nm), ZB-3(d, 100 nm & e, 50 nm), ZB-4(g, 50 nm & h, 100 nm) and ZB-5(j, 100 nm & k, 100 nm); statistical histogram ZB-2 (c), ZB-3 (f) ZB-4 (i) and ZB-5 (l).

3.2. The influence of thermodynamic parameters on the particle size of the products

TEM images in Fig. 4 show the difference between the particle size and the size distribution of ZrB_2 particles when the molar ratio of raw materials is $ZrCl_4$: B_2O_3 : Na = 1:2:4. It is clearly seen that based on the thermodynamic results of main equation, this is a spontaneous and exothermic one occuring at the same time[17]. In the present research, according to the amount of Gibbs free energy (ΔG) and the enthalpy of the reaction (ΔH) at different temperatures (see Table 2), by increasing the reaction temperature, the sintering temparature comes down causing a decrease in the particle size. If the reducing agent is strong and its concentration is high, the size of the resulting nanoparticles will be small. Generally speaking, the size and shape of the produced nanoparticles depends upon the experimental conditions (reaction time, additives, precursor nature, concentrations, and byproducts). Reducing agent influences the size of nanoparticles

as they are the driving force behind the reaction. If the reaction driving force is high, the reaction rate is greatly accelerated. High melting point temperature of the by-product produces a separation layer which inhibits the attraction force between individual particles [18]. Therefore, the growth process of the nanoparticles is greatly diminished causing the prepared nanoparticles to have small sizes (see Fig. 5). It is a well-known fact that the kind of metal selected as reducing agent can have a great effect on the growth regularity and phase composition products in the synthesis process. The melting temperature of Na metal is 98 °C. Lower melting temperature of Na brings about higher diffusion speed of the metal in the reaction matrix. Raw materials are first dissolved in this matrix; which process reduces the generating temperature of ZrB_2 powders increasing their crystallinity. The results are indicated in Fig. 3, 4. Meanwhile, the viscosity of Na has an important effect on the migration rate of the atoms in the reaction ambient. The high viscosity of the salt will restrain the migration rate of the atoms in the process of reduction. Thus, the higher the viscosity, the poorer the thermal diffusivity of the product particles trapped in the reducing agent matrix, eventually causing an improvement in the dispersibility of product particles.

Table 2. Calculated thermodynamic values for preparing ZrB_2 nano-particles at different temperatures

T (°C)	ΔH (Kj)	ΔS (j/k)	ΔG (Kj)
650	-1006.778	-300.241	-729.611
750	-1001.900	-295.241	-699.825
850	-870.914	-178.642	-676.272
950	-869.449	-172.272	-658.735

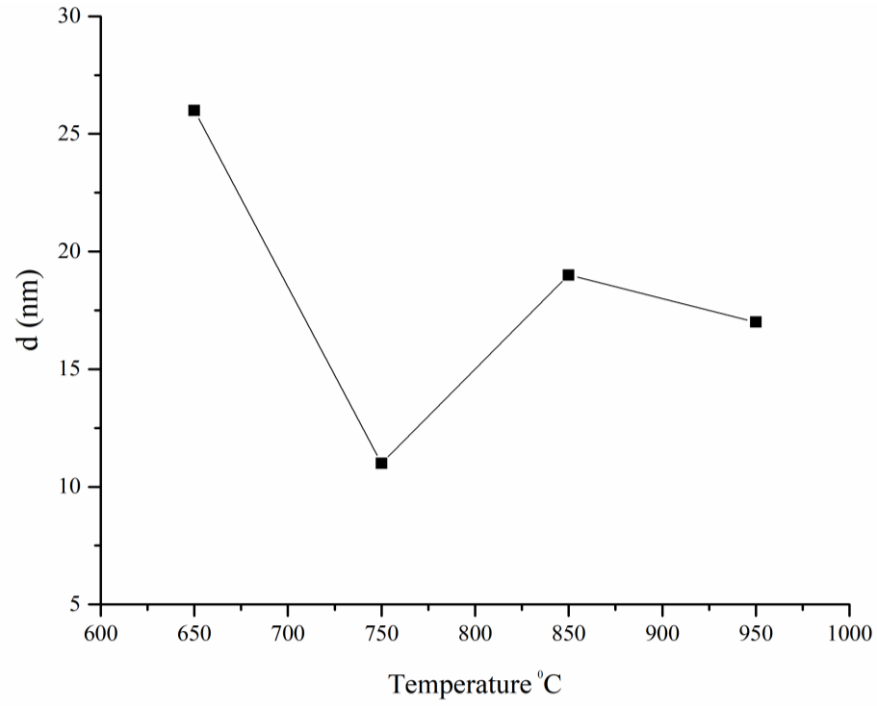


Fig. 5. Particle size values for synthesized ZrB_2 samples

3.3. The effect of adding NaCl salt in the ZrB_2 synthesis process

Table 2 indicates the reaction conditions of the products prepared at different temperatures after reacting when the NaCl-to-reactant mole ratio is 0 % and 20 %. In the sample prepared at 500 °C, the ZrB_2 phase was detected in the products but there still remained a large amount of ZrO_2. As the temperature was increased to 650,750, 850 and 950 °C, the characteristic peaks of ZrO_2 completely disappeared where all the peaks related to the ZrB_2 phase indicating that a single-phase ZrB_2 was prepared. With the assistance of NaCl salt, the temperature of the metallothermic reduction reaction decreases, this is possibly because the molten salt might greatly improve the kinetics of the reaction. When NaCl salt

was absent in the ZB-2 sample, as is shown in Fig. 2, at the beginning of the reaction, the solid reaction between $ZrCl_4$ and B_2O_3 only occurred at the contact. As the reaction proceeded, liquid B_2O_3 was generated. However, the viscosity of the B_2O_3 was much larger than that of the molten NaCl; thus, the mass diffusion through B_2O_3 was very low. When the NaCl-to-reactant mole ratio was 20 %, the molten salt acted as a mass transfer medium, which proved beneficial for the reaction of the noncontact surface of the raw materials. Consequently, the reaction could also occur at relatively low temperatures because of its favorable kinetics. Therefore, according to the results of the TEM analysis in Fig. 4, it can be seen that in sample ZB-2, due to the absence of NaCl salt, the particle sizes are relatively larger, but in samples ZB-3, ZB-4 and ZB-5, where NaCl salt is added at a certain percentage, particle sizes have grown very much smaller, indicating the salt effect on the mechanism of decreasing temperature and particle sizes.

3.3.1. Particle size decreasing mechanism

In this study, different weight percentages of dry NaCl salt were added to the reaction mixture of many of the above samples in Table 2 to investigate its effects on particle size and nanoparticle growth rate. This compound acts as an inert diluent and a dry solvent in the reaction process. The explosive nature of sodium chloride is much milder than that of other similar salts. Further, the intensity of the explosion decreases with an increase in NaCl. Typically, during ZrB_2 synthesis, molten NaCl forms a thin coating layer on ZrB_2 nanoparticles. This coating reduces the particle growth rate, indicating that ZrB_2 growth occurs at lower temperatures [19]. The presence of additives such as dry and inert salts such as NaCl as a diluent may act as a heat absorber and reduce the adiabatic temperature. Meanwhile, adding NaCl also improved the mass transfer rate by decreasing the viscosity of the liquid and provided good kinetic conditions for the crystallization process.

4. Concluding remarks

In this paper, exploiting metallothermic reduction method, ZrB_2 powder was successfully prepared at 650 to 950 ˚C after reacting for 3 h by mixing $ZrCl_4$: B_2O_3 : Metal = 1:2:4. (Metal = Na). Fine and pure ZrB_2 nano-particles were produced by making adjustments in effective factors. This eventually brought about the formation of by-products and oxide salts which were subsequently removed through washing and purification procedures. The thermodynamic data of the main equation was expressed and the effects of this parameter on the particle size were investigated. In general, for all products, the size distribution of the synthesized nano-powders was between 11 and 26 nm. The experimental results reveals that adding NaCl improves the mass transfer kinetics, accelerating the reaction, which in turn, shortens the reaction time enabling the reaction temperature to be lowered. Thus, the particle size distribution of ZrB_2, decreased by adding NaCl salt as an inert diluent. Also, the influences of thermodynamic parameters on the particle size of the products were investigated. According to the amount of Gibbs free energy (ΔG) and the enthalpy of the reaction (ΔH) at different temperatures, by increasing the reaction temperature, the sintering temperature lowers which causes a decrease in the particle size.

References

[1] M.S. Asl, B. Nayebi, Z. Ahmadi, M.J. Zamharir, and M. Shokouhimehr, Effects of carbon additives on the properties of ZrB2-based composites: A review, *Ceram. Int.*, 44(2018), No. 7, p. 7334.

[2] W.G. Fahrenholtz, G.E. Hilmas, I.G. Talmy, and J.A. Zaykoski, Refractory diborides of zirconium and hafnium, *J. Am. Ceram. Soc.*, 90(2007), No. 5, p. 1347.

[3] F. Monteverde, R. Savino, and M. De Stefano Fumo, Dynamic oxidation of ultra-high temperature ZrB2–SiC under high enthalpy supersonic flows, *Corros. Sci.*, 53(2011), No. 3, p. 922.

[4] Z. Amirsardari, R.M. Aghdam, M. Salavati-Niasari, and S. Niasari, enhanced thermal resistance of GO/C/phenolic nanocomposite by introducing ZrB2 nanoparticles, *Composites Part B*, 76(2015), p. 174.

[5] F. Monteverde, A. Bellosi, and S. Guicciardi, Processing and properties of zirconium diboride-based composites, *J. Eur. Ceram. Soc.*, 22(2002), No. 3, p. 279.

[6] S.Q. Guo, Densification of ZrB2-based composites and their mechanical and physical properties: A review, *J. Eur. Ceram. Soc.*, 29(2009), No. 6, p. 995.

[7] Y. Zhang, R. Li, Y. Jiang, B. Zhao, H. Duan, J. Li, and Z. Feng, J. Solid State Chem. 184 (8) (2011). 2047.

[8] G. H. Liu, J. T. Li, and K. X. Chen, Advances in Applied Ceramics. 112 (3) (2013) 109- 124.

[9] Gadakary Saikumar, Asit K. Khanra, and R. Veerabau, Advances in Applied Ceramics.113 (7) (2014) 419- 426.

[10] W.M. Guo, G.J. Zhang, Reaction processes and characterization of ZrB_2 powder prepared by

boro/carbothermal reduction of ZrO_2 in vacuum, J. Am. Ceram. Soc. 92 (2009) 264-267.
[11] C.W. Bale, E. Bélisle, P. Chartrand, S.A. Decterov, G. Eriksson, K. Hack, I.H. Jung, Y.B. Kang, J. Melançon, A.D. Pelton, C. Robelin, and S. Petersen, FactSage thermochemical software and databases — recent developments, *Calphad*, 33(2009), No. 2, p. 295.
[12] W. M. Guo, G. J. Zhang, L. Silvestroni, New borothermal reduction route to synthesize submicrometric ZrB_2 powders with low oxygen content, J. Am. Ceram. Soc. 94 (2011) 3702-3705.
[13] J.K. Sonber and A.K. Suri, Adv. Appl. Ceram., 110, (2011).321-334.
[14] R.A. Andrievskii, S.E. Kravchenko, S.P. Shilkin, Inorg. Mater. 31 (1995) 965.
[15] H. Kobayashi, M. Katoh, Y. Kamiyama and T. Mitamura, J. Ceram. Soc. Jpn, 100, (1992). 172-177.
[16] H. Morito, K.Koshijib, H. Yamaneb, Low-temperature synthesis of ZrB_2 powder from oxides using Na, J. of Asian Ceramic Societies 5 (2017) 479-481.
[17] Outokumpu HSC. Chemistry for Windows, v 6.0. Outokumpu Research on Information Service, Pori.
[18] H. Zhu, H. Li, H. Song, Sh. Liao**.** Front. Chem. China, 4(2) (2009) 154–159.
[19] **S**. Gadakarya, M. J. Davidsonb, R. Veerababuc, A.K. Khanra, J. Min. Metall. Sect. B-Metall. 52 (1) B (2016) 69–76.